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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003902311 for a patent by INTEC LTD as filed on 02 May 2003.



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JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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PROVISIONAL SPECIFICATION

Applicant(s):

INTEC LTD

Invention Title:

REMOVING CONTAMINANTS FROM SULFIDIC MATERIALS

The invention is described in the following statement:

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REMOVING CONTAMINANTS FROM SULFIDIC MATERIALS**Field of the Invention**

The present invention relates to a method for removing a contaminant from a sulfidic material. The present invention also relates to the recovery of product (eg. economically valuable metals) from a sulfidic material.

The present invention has been primarily developed for removing environmentally hazardous contaminants, such as arsenic, antimony and bismuth, from sulfidic materials, especially pyritic ores. In this regard, the invention can be applied to contaminated sulfidic materials having a high carbon content (a so-called "double-refractory material") or no or low carbon content (a so-called "single-refractory material") and will be described with reference to such applications. In addition, the invention allows for the recovery of precious metals such as gold, silver etc. which may be present in the contaminated sulfidic material. However, it should be appreciated that the invention has broad application to a wide variety of sulfidic ores, not only for metal recovery, but also in the processing of waste materials and residues for subsequent disposal.

Background to the Invention

Across the world there are significant deposits and quantities of sulfidic materials including economically desirable metals to recover, especially precious metals such as gold and silver. For example, there are significant deposits and stockpiles of pyritic ores including gold and/or silver and other precious metals, however a number of these deposits are contaminated with difficult to process contaminants such as arsenic, antimony, bismuth or other heavy metals. Ore treatment may also be complicated when high levels of carbon are present, as carbon associates with and has a high affinity

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for precious metals such as gold.

Where a sulfidic material includes a contaminant such as arsenic, the use of conventional smelting or roasting techniques to treat the material for metal recovery result in the formation of eg. arsenic trioxide which is difficult to collect and highly toxic so should not be released to the environment. Also, high levels of sulfur in a smelting or roasting feed produces high levels of sulfur dioxide and other SO_x gases in the exhaust.

US6461577 discloses a process for treating sulfidic materials containing arsenic where the sulfidic material is subjected to a two-stage bio-leaching process to solubilise the arsenic. The configuration of the leaching process is complex, as is the use of bio-leaching bacteria. In addition, bio-leaching is notoriously slow.

It would be advantageous if an alternative hydrometallurgical process could be provided for treating contaminated sulfidic ores and concentrates, with the attendant advantages of hydrometallurgical processing (including process simplicity, absence of emissions, lower energy requirements etc.).

Summary of the Invention

In a first aspect the present invention provides a method of removing a contaminant from a sulfidic material comprising the steps of:

•mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and
•removing the contaminant from the solution whilst regenerating the multi-valent species to its relatively high oxidation state.

Advantageously, by removing the contaminant whilst regenerating the multi-valent species, the method can be operated in a closed loop or recycle mode with attendant

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economic benefits (eg. simplicity, low energy consumption, preservation of mass balance etc.).

In a second aspect the present invention provides a method of removing a contaminant from a sulfidic material comprising the steps of:

- 5 •mixing the material in an aqueous solution having an oxidation potential controlled to oxidise substantially only the contaminant to render it soluble in the solution, thereby producing a contaminant refined material; and
- 10 •separating the solution from the contaminant refined material.

Advantageously, by controlling the oxidation potential the method enables the contaminant to be maintained in a soluble form, thus facilitating subsequent removal (eg. in a separate precipitation step). For example, where the material is an arsenopyrite and the contaminant is arsenic, the oxidation potential can be controlled such that the arsenic is oxidised to its +3 oxidation state rather than its relatively less soluble +5 state. Once the arsenic has been solubilised and separated the remaining pyrite component can then be oxidised more vigorously in a subsequent stage.

The terminology "contaminant refined material" includes a material in which contaminant has not been completely removed therefrom, but which has sufficiently low contaminant levels such that it can be acceptably further processed (eg. in roasters and smelters) or meets acceptable environmental standards for disposal etc.

The inventors have also observed that the method of the first and second aspects can be applied to otherwise difficult to treat ores and concentrates including arsenopyrites, especially double-refractory ores having a high carbon content.

Preferably the contaminant is removed from the solution by precipitation in a separate precipitation stage by introducing an oxidant into the solution.

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Preferably the oxidant simultaneously causes the multi-valent species to be oxidised to its relatively high oxidation state. Preferably after precipitating and removing the contaminant and regenerating the multi-valent species to its higher oxidation state, the solution is recycled to the leaching stage.

Preferably in the precipitation stage the solution pH is maintained at around pH 1.5-3. Preferably the solution pH is maintained by regulating the supply to the solution of the oxidant and/or an alkali agent. When addition of an alkali agent is required an alkali salt such as calcium carbonate, calcium oxide, sodium carbonate, sodium bicarbonate etc. is typically added.

Typically in the precipitation stage the oxidant causes the contaminant to precipitate by oxidising it to a relatively less soluble form (eg. oxidising arsenic from its +3 to +5 oxidation state), and at the same time oxidises the multi-valent species. Typically the oxidant is air, oxygen, chlorine gas, hydrogen peroxide etc. In pyritic ores the contaminant typically precipitates as an iron/contaminant-oxidate form (eg ferric arsenate when the contaminant is arsenic).

Preferably after contaminant precipitation, solution Eh and pH are restored to levels required for contaminant leaching, to enable solution recycle to the leaching stage. This can be achieved by eg. regulating the addition of oxidant after contaminant precipitation.

Preferably the contaminant is oxidised in a single or multi stage leaching process.

Preferably the leaching process comprises a first leaching stage in which the oxidation potential is controlled to oxidise substantially only the contaminant to render it soluble in the solution, and a second leaching stage in which the oxidation potential is increased to oxidise sulfide in the contaminant refined material. In this regard, preferably a bulk of contaminant is oxidised and solubilised in the first leaching stage

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with residual contaminant being oxidised in the second leaching stage.

Each leaching stage may be operated co- or counter-currently and in this regard, each stage may comprise one or more vessels.

Preferably the contaminant refined material that is separated from the solution after the first leaching stage is fed to the second leaching stage.

Preferably the solution is separated from the contaminant refined material after each leaching stage for removal of contaminant therefrom, typically by precipitation in the precipitation stage.

Preferably when the sulfidic material is a pyritic material (and noting that "pyritic" includes arsenopyrite and other contaminated pyrites), in the first leaching stage the contaminant is oxidised in a highly acidic aqueous solution of pH typically less than 1, at a solution Eh sufficient to oxidise the contaminant into solution but not substantially leach pyrite, preferably at an Eh of around 0.5 volts, and preferably at a temperature of about 105°C.

Preferably in the second leaching stage the pyritic material is also oxidised in a highly acidic aqueous solution of pH typically less than 1, but at a higher solution Eh sufficient to leach pyrite, preferably at an Eh of around 0.6 volts, and at a temperature of about 105°C. To achieve the higher solution Eh in the second leaching stage, typically an oxidant such as oxygen, air, chlorine gas, hydrogen peroxide etc. is added to the solution and, as necessary, an acid such as sulfuric acid may be added.

In this regard, in the second leaching stage, to maintain a low solution pH and thereby solubilise arsenic which is now present in its +5 oxidation state, the addition thereto of an acid may also be required, such as sulfuric acid, hydrochloric acid or any other acid which does not interfere with the process chemistry. However,

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the addition of an acid may not be required (eg. where sulfur present in the ore or concentrate is oxidised and thereby generates sufficient sulfuric acid in the solution).

- 5 Most preferably the solution employed throughout the leaching and precipitation stages (which is typically recycled in the overall process) is a dissolved metal chloride solution, typically having a chloride concentration of approximately 7 moles per litre. The
- 10 method is preferably operated such that the metal in the dissolved metal chloride solution functions as the multi-valent species (however a multi-valent species may be separately added to the leaching process solution). In this regard, typically the metal in the metal chloride
- 15 solution is copper, but may also be iron etc. The multi-valent species effectively acts as an electron transfer agent. For example, in the solution recycled to the leaching stage the metal is in its relatively high oxidation state (eg. Cu(II) or Fe(III)) and after
- 20 oxidation is in its relatively lower oxidation state (eg. Cu(I) or Fe (II)). However, other multi-valent species may be employed including possibly cobalt, manganese and vanadium.

- 25 As stated above, typically the sulfidic material is a pyritic ore or concentrate, and typically the contaminant is arsenic, antimony, bismuth, mercury, cadmium, which occur naturally in many as-mined sulfidic materials.

- 30 A number of pyritic ore deposits around the world have a high carbon content and, when a high level of carbon is present in the sulfidic material (eg. 2-20 wt% carbon), a surfactant such as a blinding agent can advantageously be added to the solution during the contaminant oxidation (leaching) step to prevent any
- 35 dissolved metals (especially precious metals such as gold) from adsorbing onto carbon in the material. The blinding agent is typically one or more organic solvents including

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kerosene, phenol ethers, etc. The use of a blinding agent may obviate the need for roasting to separate the precious metal from the carbon.

Preferably, after precipitating and removing the contaminant and regenerating the multi-valent species to its relatively high oxidation state, the solution is recycled to the leaching stage. Recycling the solution to the leaching stage is desirable for overall process economics and is advantageous because the multi-valent species is regenerated to its original (pre-leaching) oxidation state, and thus is ready to participate in further oxidation and leaching.

In a typical application of the present invention, the sulfidic material includes, in addition to the contaminant, a metal to be recovered. In this regard, the method preferably further comprises a metal recovery stage to recover metal from the separated contaminant refined material.

In the case of a double-refractory ore, preferably the metal recovery stage is provided as a separate, subsequent stage, to recover metal present in contaminant refined material solids from the leaching process. In this regard, where the double-refractory ore includes carbon, preferably the metal to be recovered (eg. gold) passes with the carbon through the leaching process.

In the case of a double-refractory ore, an additional in-line metal recovery stage may be provided subsequent to contaminant precipitation (ie. intermediate to contaminant precipitation and recycle to the oxidation stage) or prior to contaminant precipitation (ie. intermediate to contaminant oxidation and precipitation) to remove any metal that is solubilised or present in the solution separated from the leaching stage. Use of the terminology "in-line" refers to a stage located on the solution circuit (ie. as a result of solution recycle from contaminant removal (precipitation) to leaching).

Also, in the case of a double refractory ore, because the contaminant has been substantially removed from the sulfidic material during leaching, the metal recovery stage may comprise a conventional roasting or smelting process. Optionally chlorine or cyanide leaching may be employed after roasting to recover any remaining metal in the roasted solids material (for example, where the metal is a precious metal such as gold).

In the case of a single refractory ore (eg. where carbon is not present at all or in any significant quantity, or where the metal is not associated with carbon) preferably the metal recovery stage is provided in-line and subsequent to contaminant precipitation, but may also be provided prior to contaminant precipitation. In this regard, preferably metal recovery involves adsorption of the metal in solution onto carbon in a carbon column, typically activated carbon. Alternatively, other metal recovery processes may be employed including ion exchange, solvent extraction, etc.

Typically the metal to be recovered is a precious metal such as gold, silver, platinum or other platinum group metals, the recovery of which metal typically justifies the process economics. However, other economically significant metals may alternatively or additionally be recovered including copper, nickel, zinc, lead etc. In addition, in certain applications the contaminant may itself be desirable or necessary to recover. For example, the contaminant may be economically valuable or environmentally harmful, prompting its recovery from the contaminant precipitate (eg. this may be the case for a contaminant such as antimony, bismuth, cadmium etc.). When the contaminant constitutes the "metal" to be recovered, a recovery stage can additionally or alternatively be provided after contaminant precipitation.

Preferably, prior to metal recovery, the method further comprises a number of material separation stages

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to separate the contaminant refined material from the solution. In this regard, preferably after the first leaching stage the solution is subjected to a thickening stage to thicken and separate contaminant refined material from the solution. Preferably after the second leaching stage the contaminant refined material is filtered from the solution, however other separation methodologies may be employed such as solid/liquid settling, solution evaporation, centrifugation etc.

Thus, typically the separated solution after each of the first and second leaching stages is passed to contaminant recovery, whereas the separated refined material is typically passed to metal recovery (double-refractory) or disposal (single-refractory).

After the contaminant precipitation stage, preferably the method further comprises a contaminant separation stage to remove the contaminant from solution prior to in-line metal recovery, and prior to recycling the solution to the leaching stage. In this regard, a solid/liquid separation stage is preferably employed after contaminant precipitation. Typically this solid/liquid separation stage is facilitated by filtration, but again other separation methodologies may be employed.

In a third aspect, the present invention provides a method of removing arsenic from a gold-bearing pyritic material comprising the steps of:

- leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution in which the metal has a relatively high oxidation state, such that the metal oxidises the arsenic to render it soluble in the solution, produces a pyritic material refined of arsenic, and is reduced to a relatively lower oxidation state;

- precipitating and separating the arsenic from the solution in a precipitation stage whilst simultaneously regenerating the metal to its relatively high oxidation state; and

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•returning the solution to the leaching stage with the metal in its relatively high oxidation state.

In a fourth aspect, the present invention provides a method of removing arsenic from a gold-bearing pyritic material comprising the steps of:

- 5 •leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution having an oxidation potential controlled to oxidise substantially only the arsenic to render it
- 10 soluble in the solution, thereby producing a pyritic material refined of arsenic; and
- separating the solution from the refined pyritic material.

In a fifth aspect the present invention provides a method of treating a relatively high carbon content sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of:

- leaching the material in an aqueous solution wherein the contaminant and metal are solubilised in the solution,
- 20 whilst masking the carbon in the material to prevent precious metal adsorption thereon; and
- recovering the precious metal from the solution.

When the term "relatively high carbon content" is used herein it refers to a carbon content in the sulfidic material that is typically higher than about 2 wt%.

Preferably, the carbon is masked by adding a surfactant such as a blinding agent (as defined above) to the solution during leaching.

Typically the method of the third, fourth and fifth aspects is otherwise as conducted in the first and second aspects of the invention.

Brief Description of the Drawings

Notwithstanding any other forms which may fall within the scope of the present invention, preferred forms of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

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Figure 1 schematically depicts a generalised process flow diagram illustrating removal of a contaminant from a sulfidic material, with associated recovery of precious metal from the sulfidic material;

5 Figure 2 schematically depicts a process flow diagram for a preferred method of removing a contaminant from a single-refractory sulfidic material and recovery of precious metal from the sulfidic material;

10 Figure 3 schematically depicts a process flow diagram for a preferred method of removing a contaminant from a double-refractory sulfidic material and recovery of precious metal from the sulfidic material; and

15 Figure 4 is a graph plotting various first stage (arsenic) leaching solution parameters against time (duration of reaction); and

Figure 5 is a graph plotting various second stage (pyrite) leaching solution parameters against time (duration of reaction).

20 Modes for Carrying out the Invention

Prior to describing preferred methods of the invention by way of detail and example, a preferred method according to the present invention will first be described in overview with reference to Figure 1.

25 Referring to Figure 1, a precious metal concentrate 10 for feeding to the process is prepared by mining, milling and then flotation of a sulfidic ore. The concentrate may be a gold-containing arsenopyrite of high carbon content (eg. 2 to 20 wt% carbon) or may have low or
30 no carbon content (eg less than 2 wt%). The concentrate is ground in a ball mill 12 and is then fed to a contaminant oxidation stage in the form of arsenic leaching process 14.

35 The preferred arsenic leaching process is described below in greater detail with reference to Figures 2 & 3 and Examples 8 & 9. Leaching may be conducted in a single stage (eg. having one or more processing units, vessels or

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tanks), but typically is conducted in a multi (two) stage process. Each stage can have one or more processing units, vessels or tanks operated in a co-current or countercurrent leaching configuration, and employing over and underflows (as is known).

In either case, in the leaching process 14 a highly acidic environment is maintained (preferably less than pH 1, as leaching of arsenic from arsenopyrite is favoured by low solution pH). The acid environment can be achieved solely by the oxidation of the sulfidic material (eg. where sulfur in the material is oxidised in solution to sulfate) and/or a non-contaminating acid may be added (such as sulfuric or hydrochloric acid).

Also, in accordance with the invention the leaching solution Eh is typically maintained at greater than 0.4 volts (see Figure 4) to solubilise the contaminant. As described below with reference to Figures 2 & 3 and the Examples, preferably the leaching process has two stages. In a first leaching stage the solution Eh is carefully controlled to promote oxidation and solubilisation of arsenic in its +3 oxidation state rather than its relatively less soluble +5 state, whilst not substantially oxidising pyrite in the arsenopyritic material. In a second leaching stage an oxidant (such as oxygen, air, chlorine, hydrogen peroxide etc) is added to raise the solution oxidation potential and thereby oxidise the pyrite (which at the same time oxidises any remaining arsenic to its +5 oxidation state). To maintain As(V) in solution in the second leaching stage an acid (such as sulfuric acid) may need to be added to lower the solution pH sufficient to solubilise the arsenic.

The process solution is typically an aqueous cupric chloride solution, preferably having a chloride concentration of 7 moles/litre. In the leaching stage the cupric ion oxidises the sulfidic material to leach the arsenic etc. into solution. At the same time, the cupric ion is reduced to cuprous ion. Thus, in the process, the

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copper acts as an electron transfer agent. Other agents can perform this function, including iron, cobalt, manganese, vanadium, etc.

Where the sulfidic material has a high carbon content (eg. greater than 2 wt%) a masking surfactant may be added to the solution at stage 14 to prevent adsorption onto carbon of any precious metal leached into the solution. The surfactant is typically an organic blinding agent such as kerosene, a phenol ether etc.

The present inventors have surprisingly found that at an acid pH less than 1, and at a controlled Eh (oxidising potential) in the range of from 0.4 to 1.25 volts, in fact optimally at around a relatively modest oxidising potential of 0.5 volts, arsenic can be oxidised and leached into solution in its relatively soluble +3 oxidation state, and without oxidising pyritic sulfide to sulfate.

In a first leaching stage the arsenopyrite concentrate is leached for a predetermined period of time (as described below in the Examples) until a predetermined amount of arsenic has been leached out of the arsenopyrite material (typically around 85% of total in the first leaching stage and an additional 10% of total in a second leaching stage). In any case, the amount leached is typically determined by acceptable residual levels in the leached arsenopyrite material, assuming that it is to be separated and subsequently processed by conventional smelting or roasting techniques, or disposed of (as described below). The term "refined arsenopyrite" or "refined sulfidic material" is thus to be interpreted in this regard.

In accordance with the invention, the solution pH and solution Eh are regulated such that arsenic and the multi-valent species Cu(II) (which oxidises and leaches the arsenic from the material) remain in solution and do not precipitate therefrom in the first leaching stage. In addition, the process operating conditions are controlled

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such that the arsenic is maintained in solution during solid/liquid separation (which separates the refined arsenopyrite from the solution) until the solution is fed to an arsenic precipitation stage.

5 Thus, after leaching the solution (leachate) is separated from the refined arsenopyrite. In Figure 1 this is depicted schematically as a thickening stage 16. In Figures 2&3 this thickening stage is employed after a first leaching stage (described below). In thickening
10 stage 16 the refined arsenopyrite solids are flocculated (ie. by adding thereto a flocculating agent), with the solids dropping out as an underflow stream 18 and the arsenic pregnant supernatant solution passing out of the thickening stage as an overflow stream 20. In Figure 1
15 the underflow or slurry 18 is then passed to a solid-liquid separation stage 22, where typically the solids are filtered from the solution using known filtering apparatus.

The resulting liquid filtrate 24 is returned to
20 overflow stream 20, whereas the filtered solids (ie. refined arsenopyrite) 26 are passed to a conventional roasting stage 28 and conventional cyanide leaching stage 30 for recovery of gold product 32.

Depending on the degree of leaching of precious metal
25 in arsenic leaching stage 14, some gold may pass with combined liquid stream 34, being the combination of streams 20 and 24, and be recovered in an in-line precious metal recovery stage 36. The recovery stage may comprise one or more columns filled with activated carbon through
30 which the solution is passed upwardly, such as in a fluidised bed arrangement. Dissolved gold (or other precious metal) in the solution adsorbs onto the carbon, whilst the dissolved arsenic in solution passes through the column as an overflow liquid stream 38. The activated
35 carbon bearing gold is then removed periodically and passed as a gold product stream 40 (together with gold

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product stream 32) to a gold recovery process (eg. by burning or eluting the carbon product).

From metal recovery stage 36, the solution 38 (including dissolved arsenic) is passed to a contaminant precipitation stage in the form of arsenic precipitation stage 42. Stage 42 is typically operated at pH 1.5-3. In stage 42 an oxidant is introduced (eg. sparged) into the solution (eg. as air, oxygen, chlorine etc.) to raise the solution oxidising potential (Eh), causing the dissolved arsenic to form a precipitate (typically arsenic forms an insoluble ferric arsenate precipitate (ie. FeAsO_4 or scorodite) in this pH range). Where the contaminant includes eg. antimony, the contaminant can assume the insoluble form ferric antimonate. However, as the contaminant precipitate forms, an acid is typically generated. Thus, addition of an alkali may be required to consume acid and maintain optimum solution pH and Eh. Typically the alkali is an alkali salt such as calcium carbonate, calcium oxide etc.

Thus, in further accordance with the invention the addition of oxidant and alkali is regulated to maintain optimum pH and Eh levels in the contaminant precipitation stage until all contaminant is precipitated. Thereafter, the solution pH and Eh levels are preferably restored to those of the leaching stage 14, so that after contaminant precipitation the solution can be recycled to that stage.

Also, in accordance with the invention, in the precipitation stage the oxidant causes the cuprous copper to be oxidised to cupric copper, thus regenerating this species and allowing for its recycle and reuse. In other words, advantageously, the regulation of solution Eh and pH promotes the re-oxidation of the multi-valent species whilst maintaining it in solution at all times so that, in the overall process, copper alternates between its +1 oxidation state and +2 oxidation state). In other words, the multi-valent species functions in the process as an electron transfer agent and, when the solution is recycled

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to the arsenic leach stage, the multi-valent species is ready to participate in further contaminant oxidation (leaching). Regeneration of the multi-valent species enhances the process economics, simplifies the process and allows the process mass balance to be completed.

After arsenic precipitation, the solution includes entrained arsenic precipitate. The solution is separated from the arsenic precipitate in a solid/liquid separation stage. In Figure 1 this is depicted schematically as a further thickening stage 44, to produce a solids (arsenic precipitate) underflow 46, which is then passed to a solid-liquid separation stage 48. A supernatant liquid overflow stream 50 is passed out of the top of the thickening stage 44. In the solid liquid separation stage 48, typically the arsenic precipitate is filtered out using a filtration apparatus, producing a waste arsenic product 52. The liquid filtrate is returned to the overflow stream 50 as liquid flow 54. The combined liquid stream 56 is then passed to a further precious metal recovery stage 58, for example, an activated carbon column etc to recover any metal not recovered at stage 36. Alternatively stage 58 can be used instead of stage 36. The resultant precious metal and activated carbon stream 60 is combined with the other precious metal recovery streams 40 and 32, whilst a solution overflow 62 is recycled to the arsenic leaching stage 14 to close the process recovery loop.

Optionally, depending on whether or not there is contaminant build up in the overall process, a proportion of the recycle stream 62 may be recycled to a bleed circuit 64 to separate out any contaminant not recovered in the arsenic precipitation stage and optionally any other contaminants such as Mn, Cd, Ni, Co etc.

Now that the process has been described in overview, preferred process flowpaths will be described with reference to Figures 2 & 3.

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Figure 2 shows a process flowsheet for the treatment of a single-refractory sulfidic material. In Figure 2, like reference numerals are used to denote similar or like process stages to that of Figure 1. In a similar manner to Figure 1, a gold-bearing arsenopyritic concentrate of low or no carbon content (i.e. single-refractory) is prepared and ground 10,12. The ground concentrate is then fed to a preferred leaching process in accordance with the present invention. The preferred leaching process has two stages, namely, a first arsenopyritic (FeAsS) leaching stage 70 and a second pyritic (FeS_2) leaching stage 72.

The arsenopyritic concentrate is thus fed to first leaching stage 70 wherein the leaching conditions are controlled such that substantially only the arsenic in the concentrate is oxidised and leached into solution and not the pyritic component of the concentrate. In this regard, the leaching conditions in first leaching stage 70 are controlled such that the oxidation potential E_h is around 0.5 volts, the solution pH is less than 1, and the solution temperature is maintained at about 105°C (although can be operated in a range between 80°C and 105°C). These conditions were observed by the inventors to be optimal for the leaching of arsenic into solution in its soluble +3 oxidation state from an arsenopyritic concentrate. As discussed below in Example 8, after about 6 hours of leaching, approximately 85% of the total arsenic in the arsenopyritic concentrate was leached into solution in its +3 oxidation state.

Once a predetermined amount of arsenic has been leached into solution, the solution and concentrate (i.e. arsenic refined arsenopyrite) is passed to a thickening stage 16 in a similar manner to the process described in Figure 1. Refined arsenopyrite solids are flocculated and drop out as underflow stream 18, whereas the arsenic pregnant supernatant solution passes out of the thickener as overflow stream 20 to arsenic precipitation stage 42.

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In accordance with the present invention the refined arsenopyrite solid stream 18 is now passed to the second leaching stage 72 for leaching of pyrite. The oxidising conditions in the second leaching stage are more severe than the first leaching stage. In this regard an oxidant such as oxygen is sparged into the solution so that the oxidation potential EH is increased to approximately 0.6 volts. In addition, the temperature of the solution in the second leaching stage is maintained at around 105°C. The pH of the solution in the second leaching stage is maintained at less than pH 1.

Because acid is consumed in the second stage leaching process (ie. as Cu(II) and Fe(III) are reduced to Cu(I) and Fe(II) respectively) it may be necessary to periodically or continuously supply acid to the solution, such as sulphuric acid, hydrochloric acid or another acid that does not interfere with the process chemistry. However, the top-up of acid depends on whether sufficient sulfuric acid is produced by the leaching of pyrite. Maintaining low pH in the second leaching stage also helps solubilise As(V).

In any case, in the second leaching stage sulfide is oxidised through to sulfate, iron is leached into solution as Fe(III) and a proportion of any remaining arsenic in the arsenopyritic ore is also leached into solution. The inventors have observed that a further 10% of the total arsenic can be leached into solution, such that final residual arsenic from the leaching process is at 5% of total in the concentrate feed. This equates with arsenic levels that are sufficiently low for the residues from the process to be safely disposed of.

The leachate from second leaching stage 72 is passed as a stream 74 to a solid-liquid separation stage 22, similar to Figure 1, where the residual solids are filtered from the solution and a liquid filtrate stream 24 is returned to and combined with overflow stream 20 for passing to arsenic precipitation stage 42. Solid residues

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filtered out at stage 22 are then passed to tails as stream 76, either as filtered solids or as a slurry. In this regard, water may be added at stage 22 to maintain water levels in the process and/or to top up water that is lost with the process residue.

In further accordance with the present invention, gold or other precious metal is often present in the single refractory arsenopyritic material and pyritic material. Because the gold or precious metal is not associated to any significant extent with carbon in the single refractory material it may thus be leached into solution in both the first and second leaching stages and can therefore be recovered in the process circuit. However, prior to gold or other precious metal recovery, arsenic (or like contaminant) is removed from the process solution in arsenic precipitation stage 42.

In this regard, and as described above, the pH of the solution is adjusted to approximately 2 to 3 (e.g. by the addition of calcium carbonate), and an oxidant such as air or oxygen is added to the solution to oxidise the arsenic from its soluble +3 state to its insoluble +5 state. Advantageously, because Fe(III) is present in the solution from the oxidation of pyrite in the second leaching stage, the arsenic precipitates out as scorodite (FeAsO_4). As a further advantage, because sulfide has been oxidised to sulfate in the second leaching stage, the addition of calcium carbonate can be used both to raise the solution pH in the arsenic precipitation stage, and to precipitate out the sulfate as calcium sulfate.

The arsenic and solids precipitate together with the process solution is then passed as stream 78 to solid-liquid separation stage 48 where the solids are filtered from the solution. The solids residue stream 80 typically comprises FeAsO_4 , Fe_2O_3 and CaSO_4 in a form suitable for disposal (e.g. as landfill). Once again, the solids may be removed as a slurry and hence water may be needed to be added to the process at stage 48. Thus, the preferred

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method according to the invention advantageously enables removal of arsenic, iron and sulfur in readily disposable forms from an original arsenopyrite concentrate.

- Furthermore, the conditions in the arsenic precipitation stage do not affect the precious metal leached into solution in the leaching stage and thus the separated solution 56 can now be passed to a precious metal recovery stage 58, in a similar manner to the process of Figure 1. Typically stage 58 comprises one or more columns housing activated carbon onto which the precious metals, typically gold, are adsorbed. Periodically a gold product stream 60 is removed from stage 58 for gold recovery (by burning or eluting the carbon with adsorbed gold thereon).
- As in the process of Figure 1, the solution overflow 62 from stage 58 is recycled to the leaching process, and a proportion of the recycled stream may be drawn off to bleed circuit 64 to separate out the contaminants which can build up in the process, thereby producing contaminant by-product stream 82.

- In further accordance with the invention, solution recycle 62 is split to produce a first leaching stage recycle component 84 and a second leaching stage recycle component 86. Where the basic process solution is e.g. a copper chloride solution, copper in its +2 oxidation state is recycled to each of the leaching stages to participate in arsenopyritic leaching in the first leaching stage and pyrite leaching in the second leaching stage.

- Referring now to Figure 3 a process flowsheet for the treatment of a double-refractory sulfidic material is shown. In Figure 3, like reference numerals are used to denote similar or like process stages to that of Figures 1 and 2. In addition, the upper half (ie. above the dotted line) of the process flowsheet of Figure 3 is essentially the same as that of Figure 2 and hence those process stages will not be described again.

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In Figure 3, a double-refractory arsenopyritic concentrate is treated. In this case, the precious metal, typically gold, is associated with carbon and hence that associated gold is not readily leached out of the concentrate in the first or second leaching stages. Accordingly, solids stream 76 includes solid residues together with an associated carbon/gold component. However, because the leaching process has substantially removed arsenic, iron, sulfur and other contaminants to acceptably low levels, the solids residue from the leaching process is now highly suitable for roasting or smelting in roasting stage 28.

In roasting stage 28, air and fuel together with solids material 76 are roasted in a conventional manner, producing a product stream 90 which is then fed to a gold leaching stage 30 in a known manner. Gold leaching is typically conducted by oxidising the roasted solids with chlorine gas or cyanide (although chlorine gas is preferable because it is less toxic than cyanide). In further accordance with the invention, a proportion 92 of the solution recycle stream from the arsenic precipitation stage 42 is fed to the gold leaching stage 30.

An exhaust gas stream 94 from the roasting stage 28 (typically comprising carbon dioxide, sulfur dioxide and other SO_x gases) is fed to a primary gas cleaning stage 96. Primary gas cleaning stage typically comprises one or more scrubbers in which water and optionally recycled wash water are contacted with the gas stream 94. Advantageously, any dust in gas stream 94 can be filtered. Such dust may include gold chloride ($AuCl_3$) and arsenous oxide (As_2O_3). This dust and particulates can be fed as solids or in solution as a stream 98 back into the arsenic precipitation stage 42 for further recovery of arsenic and gold.

Residual gases from the primary gas cleaning stage 96 are passed as stream 100 to secondary gas cleaning stage 102, typically comprising gas scrubbers in which calcium

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carbonate in solution is contacted with the SO_x containing gases. Product stream 104 from the secondary gas cleaning stage 102 typically therefore comprises calcium sulfate and calcium sulfite.

5 The leachate stream 106 containing dissolved gold from the gold leaching stage 30 is now passed to a solid-liquid separation stage 108 to separate the gold containing solution from the solids residue. The solids residue stream 110 is passed to tails for disposal, whereas the gold pregnant solution is passed to a gold recovery stage 114, typically comprising an activated carbon containing column. Carbon and adsorbed gold is periodically removed out as stream 116 for gold recovery, whereas gold depleted solution 118 is recycled to the leaching/arsenic removal circuit to be combined with stream 34.

Examples

Now that optimal process flowpaths have been described, preferred examples of the method according to the present invention will be described. In the following examples, an arsenopyrite concentrate from Bakyrchik, Kazakhstan was processed. The aim was to develop a process that permitted processing of all samples of arsenopyrite ore provided from the Bakyrchik mine.

Example 1

Concentrate Characterisation.

Method:

6kg of concentrate was processed by ultra fine regrinding. The concentrate possessed a P₁₀₀ 20 microns

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Product	
Laser microns	Wt% passing
20	100
18	99
15	96
12	89
10	81
8	69
6	50
5	42
3	15

The concentrate at P₁₀₀ 20 microns was received in three cakes, the moisture content of each cake was determined, and the average was used as the moisture content for the concentrate.

Cake 1

Wet sample + paper: 113.84g
10 Dry sample + paper: 85.68g
Paper: 4.83g
Dry sample: 80.85g
% Moisture: 25.8%

15 Cake 2

Wet sample + paper: 88.35g
Dry sample + paper: 66.65g
Paper: 4.83g
Dry sample: 62.02g
20 % Moisture: 25.9%

Cake 3

Wet sample + paper: 86.41g
Dry sample + paper: 68.79g
25 Paper: 4.85g

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Dry sample: 63.94g

% Moisture: 21.6%

The average moisture content determined was 24.4%.

- 5 From this it was calculated that 100g of dry concentrate translated to 132.3g of the wet concentrate sample.

Example 2

Oxidation Leach

- 10 Tests were then conducted on the $P_{100} = 20$ microns reground sample to provide initial evidence of arsenic leaching via a process of oxidation. The Bakyrchik ore concentrate was noted to contain arsenic as an arsenopyrite. The reaction was designed to determine if
15 this arsenic could be rendered soluble (and hence be selectively removed) using cupric copper as oxidant.

Method:

- A 1L solution of 80g/L Cu^{2+} (as CuCl_2 205.13g),
20 100g/L CaCl_2 , 200g/L NaCl and 30g/L NaBr was prepared. 140g of wet concentrate (~24% moisture, therefore 105.8g dry concentrate) was added to this the solution and the resultant slurry stirred at 105°C. The pH, Eh and Fe and Cu content were measured over the course of four hours.
25 Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis. Solid cake was washed with low pH brine (~0.5L, 280g/L, pH 0.3), the resultant moist cake was weighed, dried in an oven and weighed again. The dry solids were preserved for
30 further analysis.

Results and Discussion:

The pH, Eh and Fe and Cu tenor recorded over time were summarised as per the table below.

35

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Time (min)	pH	Eh (mV)	Fe (g/L)	Cu ^{tot} (g/L)
0				
30	1.45	740	2.4	70.6
60	0.5	508	2.5	68
90	0.5	507	2.5	63
150	0.5	495	2.65	64
210	0.35	502	2.65	61
270	0.35	495	2.68	64
330	0.35	485	2.66	65

The residue assay shows an As concentration of 0.66%.
 Considering a calculated mass loss of 6.5%, the As was
 5 leached with an efficiency of 82.3 %

The reaction appeared to proceed quickly. A
 significant drop in Eh and pH was observed within the
 first hour of the reaction's progress. After this time the
 10 reaction stabilised and did not appear to progress
 further.

Example 3

15 Oxidation Leach

The aim of this example was to investigate whether
 fresh liquor would facilitate the further leaching of the
 iron/ arsenic from the previously leached material. It was
 surmised that treatment of the solid obtained from the
 20 previous leach would remove more of the arsenopyrite. A
 fresh solution of the primary liquor was prepared and a
 repeat of the previous leach was performed using the
 leached material as the solid feed.

25 Method:

A 500ml solution of 80g/L Cu²⁺ (as CuCl₂ 102.55g),
 100g/L CaCl₂, 200g/L NaCl and 30g/L NaBr was prepared. 30g
 of the leached concentrate obtained from the previous

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oxidation was added to this solution and the resultant slurry stirred at 105°C. pH and Eh were measured over the course of four hours. Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis. Solid cake was washed with low pH brine (~0.5L, 280g/L, pH 0.3), the resultant moist cake was weighed, dried in an oven and weighed again. The dry solids were preserved for further analysis.

Samples taken from the solids obtained from this and the previous reaction as well as the original concentrate were digested using Aqua-regia/perchloric acid. These solutions were then analysed for Arsenic using ICP.

Results and Discussion:

The pH, Eh recorded over time were summarised as per the table below.

Time (min)	pH	Eh (mV)
0	1.32	741
0	1.2	615
30	0.55	588
60	0.31	583
90	0.29	580
120	-	579
150	0.31	569
180	0.3	574
210	0.29	574
240	0.32	572

Wet cake + paper + filter paper: 72.5g
Dry cake + paper + filter paper: 40.24g
Paper + filter paper: 11.5g
Dry cake obtained: 28.74g

The ICP analysis for Arsenic in the recovered solids were summarised as per the table below:

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	As	
	Content	Extraction
	(wt %)	(%As in concentrate)
Bakyrchik concentrate	3.49	0
Leach 1	0.66	82.3
Leach 2	0.42	88.9

As was observed in the previous leach the reaction appeared to proceed quickly, stabilising over the course of an hour. A significant drop in Eh and pH was again observed along with a decrease in the mass of the solids recovered when compared to the mass of the solids fed to the solution. This suggested that there was material left in the residue from the primary leach that was still extractable. An analysis of the arsenic content of both the feed and solid residue from both leaches revealed a progressive reduction in the arsenic content of the solids recovered. The results suggested that the method could be refined to selectively leach the arsenic contained within the Bakyrchik concentrates.

Example 4

Oxidation Leach

The aim of this example was to refine the conditions used in leaching arsenic from the Bakyrchik ore. Having succeeded in leaching ~65% of the arsenic contained within the Bakyrchik ore, the method was refined to obtain a greater leach performance. The method focused on two areas: firstly the leach liquor was simplified, and secondly, the reaction was carried out at various

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temperatures and starting pH's to determine the effect these changes had on improving the leach efficiency.

5 Method:

A 5L solution of 80g/L Cu^{2+} (as CuCl_2 , 1025.64g), 150g/L CaCl_2 (750g) and 150g/L NaCl (750g) was prepared and heated to 80°C. This solution was then divided into three 1.5L solutions, each solution performing an oxidation
10 leach under different conditions on the equivalent of 142.86g wet concentrate (~24% moisture, therefore 108g dry concentrate).

15 Oxidation Leach Solution 1: Leach was performed at 80°C

Oxidation Leach Solution 2: Leach was performed at 100°C

Oxidation Leach Solution 3: Leach was performed at 80°C. Starting pH <0.4, Eh >550mV

20 The pH and Eh of these solutions was measured over the course of two and a half hours. Samples from each were taken at intervals and analysed for their iron and copper content.

25 Solids were subsequently filtered using a Buckner apparatus and the filtrate preserved for further analysis. Solid cake was washed with low pH brine (~1L, 280g/L, pH 0.3), and the resultant moist cake was weighed, dried in
30 an oven and weighed again. The dry solids were preserved for further analysis.

Samples taken from the solids obtained from each reaction as well as the original concentrate were digested
35 and analysed for arsenic, copper and iron using ICP.

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Results and Discussion:Oxidation Leach 1 (80°C) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	2.15	720				Solids added
0	1.58	568	71	-	-	
30	0.95	535	77	0.79	824	
60	0.75	525	77	1.14	1033	
90	0.70	520	75	1.28	1152	
120	0.70	520	75	1.41	1216	
150	0.70	516	74	1.53	1308	

5

Wet cake + paper + filter paper: 173.24g

Dry cake + paper + filter paper: 105.48g

Paper + filter paper: 11.5g

Dry cake obtained: 93.98g

10

Oxidation Leach 2 (100°C) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	1.88	735				Solids added
0	1.5	561	71	-	-	
30	1.1	525	79	1.75	1473	
60	1.05	528	79	1.85	1532	
90	0.98	529	80	2.0	1636	
120	0.94	525	84	2.0	1678	
150	0.89	528	85	2.14	1761	

Wet cake + paper + filter paper: 170.3g

15 Dry cake + paper + filter paper: 113.32g

Paper + filter paper: 11.5g

Dry cake obtained: 101.82g

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Oxidation Leach 3 (80°C, low pH) Solution Assays

Time (min)	pH	Eh (mV)	Cu (g/L)	Fe (g/L)	As (ppm) From ICP	Comments
0	0.35	712				Solids added
0	0.8	564	71	-	-	
30	0.55	540	76	1.06	741	
60	0.43	532	74	1.41	975	
90	0.5	525	74	1.51	1082	
120	0.4	520	75	1.61	1162	
150	0.43	515	73	1.61	1181	

- 5 Wet cake + paper + filter paper: 172.4g
 Dry cake + paper + filter paper: 108.46g
 Paper + filter paper: 11.5g
 Dry cake obtained: 96.96g

- 10 The ICP analysis for arsenic, copper and iron in the recovered solids are summarised as per the table below.

	As%	Cu%	Fe%	As% Extraction
Cons	3.22	0.09	8.38	0.0
Leach 1	1.07	0.31	5.22	71.1
Leach 2	0.25	0.30	2.85	92.7
Leach 3	1.57	0.30	5.40	56.2

- 15 These results clearly indicate that the rate of reaction is significantly higher at 100°C than at 80°C.

Example 5Iron/Arsenic Rejection process

- 20 Method:

Liquor obtained from a previous oxidation reaction (10L) was returned to the vat and heated to 80°C with low

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stirring. Upon reaching this temperature the pH and Eh of the liquor were measured and a sample taken. The liquor was then aerated (100L/hr) with agitation, and the pH and Eh of the liquor was measured and a sample was taken every thirty minutes thereafter. After four hours the rejection process was considered to be complete, the liquor was filtered using a Bucher apparatus and the rejected precipitate was removed as a filter cake. The wet cake was weighed, and then dried over twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis.

Results and Discussion:

The pH and Eh and tenor of the liquor over time were summarised as per the table below.

Time mins	pH	Eh (mV)	Sample No.	As (g/L)	Fe (g/L)	AAS Cu (g/L)	AAS Fe (g/L)	Comments
0	0.7	500	1	2.8	3.7	88	3.7	Vol:10L
0	0.7	500	-	-	-	-	-	air@100L/Hr
30	1.1	510	2	2.3	3.6	90	3.3	
60	1.5	520	3	1.2	2.7	90	2.6	
90	1.6	525	4	0.6	2.4	91	2.2	
120	2.0	530	5	0.3	1.3	85	1.6	
150	2.1	535	-	-	-	-	-	
180	2.1	545	-	-	-	-	-	
210	2.2	555	-	-	-	-	-	
240	2.5	570	6	ND	0.5	88	<0.1	Cu ^{tot} 88, Cu ²⁺ :88

Wet cake + paper + filter paper: 257.2g

Dry cake + paper + filter paper: 128.94g

Paper + filter paper: 11.5g

Dry cake obtained: 117.44g

20

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Analysis of the precipitate shows the following results:

Element	Concentration (wt %)
As	19.0%
Fe	33.8%
Cu	1.5%

- 5 Over the four hour period of the experiment, essentially
100% of both the iron and arsenic were precipitated,
whilst concurrently the oxidation potential (Eh) was
restored to a level higher enough to be used for further
leaching. The Fe/As molecular ration being 2.4, it is
10 anticipated that FeAsS was precipitated with other Fe
based compounds.

Example 6

15 Iron/Arsenic Rejection process

Method:

- Liquor obtained from the oxidation reaction (10L) was
returned to the vat and heated to 80°C with low stirring.
Upon reaching this temperature the pH and Eh of the liquor
20 were measured and a sample taken. The liquor was then
aerated (100L/Hr) with agitation, and the pH and Eh of the
liquor was measured and a sample was taken every thirty
minutes thereafter. After four hours the rejection process
was considered to be complete, the liquor was filtered
25 using a Bucher apparatus and the rejected iron precipitate
was removed as a filter cake. The wet cake was weighed,
and then dried over twenty-four hours in an oven. The dry
cake was then weighed and a sample digested for analysis.

Results and Discussion:

- 30 The pH and Eh and tenor of the liquor over time were
summarised as per the table below.

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Time mins	pH	Eh (mV)	Sample No.	As (g/L)	Fe (g/L)	AAS Cu(g/L)	AAS Fe (g/L)	Comments
0	0.7	500	1	2.8	3.7	88	3.7	Vol:10L
0	0.7	500	-	-	-	-	-	air@100L/Hr
30	1.1	510	2	2.3	3.6	90	3.3	
60	1.5	520	3	1.2	2.7	90	2.6	
90	1.6	525	4	0.6	2.4	91	2.2	
120	2.0	530	5	0.3	1.3	85	1.6	
150	2.1	535	-	-	-	-	-	
180	2.1	545	-	-	-	-	-	
210	2.2	555	-	-	-	-	-	
240	2.5	570	6	ND	0.5	88	<0.1	Cu ^{tot} 88, Cu ²⁺ :88

Wet cake + paper + filter paper: 257.2g

Dry cake + paper + filter paper: 128.94g

Paper + filter paper: 11.5g

Dry cake obtained: 117.44g

5 Moisture component: 128.26g (47.8%)

Example 7

Leach on regenerated liquor, lower slurry density

Method:

- 10 A 90g sample of wet concentrate (~24% moisture, therefore 68g dry concentrate) was added to the liquor obtained from the oxidation reaction (1.5L) and the resultant slurry stirred at 100-105°C. The pH and Eh of the liquor were monitored and a sample taken every thirty
- 15 minutes over a four hour period. After this period the liquor was filtered using a Bucher apparatus and the filter cake removed, the wet cake was weighed and then dried over twenty-four hours in an oven. The dry cake was then weighed and a sample digested for analysis.

20 Results and Discussion:

The pH and Eh and tenor of the liquor over time is summarised in the table below.

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Time (min)	pH	SH (mV)	Sample No.	AAS Cu (g/L)	AAS Fe (g/L)	ICP As (g/L)	ICP Cu (g/L)	ICP Fe (g/L)
0	2.5	600	-	-	-			
10	1.8	555	-	-	-			
30	1.5	550	1	90	1.5			
60	1.3	545	2	89	1.1			
90	1.2	540	3	87	1.2			
120	1.1	540	4	67	0.8			
150	1.1	535	5	88	1.0			
180	1.0	535	6	85	1.0			
210	1.0	535	7	88	1.0			
240	1.0	536	8	87	1.1			

Dry cake obtained: 58g

5 First & Second Leaching Stage Examples

Example 8

First Stage Leaching

In this example, the aim was to confirm through a simulation of a continuous process that the operating conditions used for batch testing would apply to a commercial operation. This experiment also provided material to be used for a pyrite oxidation at atmospheric pressure.

As shown in Figure 5, continuous operation under conditions similar to the batch processes of Examples 2 to 4 consistently delivered an As extraction of 85%.

Procedure

7.5 litre titanium reactors were employed, with the overflow from the first connected to the second, which subsequently overflowed into a holding tank. During continuous operation, 2 litres/hr of solution was fed to the first reactor from a feed tank using a peristaltic pump. The solids addition rate was 144g/h and was achieved

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through 24g (dry basis) batch additions of concentrate to the first reactor every 10 minutes.

Initially a 30 litre stock solution containing 80g/l Cu^{2+} , 200g/l NaCl, 100g/l CaCl_2 , and pH<1 was prepared. To each reactor, 7.5 l of stock solution was added and maintained at 100°C, with 360g of dry equivalent P80 - 30 microns low grade gold (30 gr/tonne) concentrate added and the resultant slurry agitated and monitored every 30 mins for Eh, pH, As, Fe and Cu. After 3 hours, a 100ml slurry sample was taken and filtered in a Buchner funnel and washed with acidic brine solution. The solids were then dried and assayed by ICP for copper, arsenic and iron.

After 3 hours, continuous operation was conducted (as described) for a further 10 hours, with a 200ml slurry sample taken every 2 hours and filtered as described above. The solids were then dried and assayed by ICP for copper, arsenic and iron.

The results are summarised in the following tables:

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Tank 1

Ref #	Solid Sample	Time (min)	Sample (#)	T (°C)	EH mV	pH	Cu (gpl)	Fe (gpl)	As (gpl)	Comments
0		0	0	95	620	1	77	0	0	
1										Added 720g dry solids
2		60	1	100	520	0.5	87	2.6	2.3	All additions below are in "as is" moist concentrate
3		120	2	100	520	0.5	83	2.7	2.3	192.95 g added over the hour
4		180	3	90	530	0.7	81	1.7	1.4	187.9 g added over the hour
5		240	4	98	535	0.6	88	1.9	1.6	183.4 g added over the hour
6		300	5	103	540	0.4	89	2.5	2.1	189.65 g added over the hour
7	1	360	6	109	530	0.2	74	2.2	1.9	195.44 g added over the hour
8		420	7	109	535	0.2	95	3.7	3.3	194.42g added over the hour
9	2	480	variable conditions							51.61g added over the hour
10		540	8	106	525	0.2	95	4.9	4.3	200g added over the hour
11		600	9	102	524	0.3	95	4.2	3.8	198.79 added over the hour
12	3	660	10	70	509	0.7	98	3.2	2.6	62.82g added over the hour
13	4	680	11	74	501	0.8	99	3	2.4	

Tank 2

Ref #	Hours	Time (min)	Sample (#)	T (°C)	EH mV	pH	Cu (gpl)	Fe (gpl)	As (gpl)
0		0	0	80	620				
1									
2		60	1	85	530	0.9	77	1.3	1
3		120	2	86	530	0.8	81	1.5	1.2
4		180	3	90	530	0.7	84	1.7	1.5
5		240	4	88	530	0.6	86	1.8	1.6
6		300	5	85	525	0.5	91	2.1	1.8
7		360	6	85	520	0.4	95	2.2	2
8		420	7	85	520	0.4	105	2.7	2.3
9		480	variable conditions						
10		540	8	84	519	0.4	99	2.8	2.5
11		600	9	83	514	0.4	98	3.2	2.9
12		660	10	83	516	0.4	98	3.5	3.1
13		680	11	83	512	0.4	99	3.9	2.94

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Solid Analysis Feed and Tank 2 overflow

Ref #	Description	Fe	As	Cu	As Extracti on	Mass Loss
		(%)	(%)	(%)	(%)	(%)
	Feed	8.60	3.20	0.08	0.00	0.00
1	Tank 2 - Solids 1	4.25	0.58	0.50	83.1	6.55
2	- Solids 2	4.15	0.42	0.52	87.8	6.79
3	- Solids 3	4.55	0.51	0.55	85.1	6.27
4	- Solids 4	4.15	0.51	0.42	85.1	6.80
mix	- Solids 5	4.50	0.52	0.42	84.8	6.44

Average

85.2 6.57

5. Example 9

Second Stage Leaching

The aim of this experiment was to evaluate the possibility of oxidising the pyrite component of the residue from an As leach, at atmospheric pressure with pure oxygen. 500 g of the residue obtained during the continuous leach test of Example 8 was used in this experiment.

The pyrite was successfully oxidised with oxygen at

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atmospheric pressure and 105 °C. The final As and Fe extraction were both above 95 %. The $S_{(e)}$ (elemental sulfur) in the oxidation residue was equivalent to the sulfur associated with the arsenopyrite in the concentrate. The results are presented graphically in Figure 6.

Procedure

A 7.5 L titanium reactor was prepared with a turbine agitator for gas dispersion and the appropriate titanium gas injector on a large yellow hotplate. 5 L of brine solution was prepared in 7.5 L titanium reactor with the following composition:

250 g/L NaCl, 50 g/L $CaCl_2$, 20 g/L Cu (from cupric chloride) and pH adjusted < 1.0.

A representative sample of dry As leach residue from Example 8 was sent to an external lab to analyse for elemental S, total S, Au, Fe and As.

With the agitator drive set at 80 Hz on the VSD, the temperature of the solution was raised to 105°C, sample t=0 is taken, Eh & pH were monitored and 500g of dry arsenic leach residue from Example 8 was introduced into the solution. After 30 minutes, a sample of solution was taken for Fe, As & Cu analysis and Eh and pH were monitored.

Oxygen was introduced at the rate of 1 L/min. Eh, pH, Fe, Cu and As were monitored every 30 minutes for the first 3 hours and every hour after that. When the soluble Fe assay stopped increasing, the experiment was considered complete.

The last sample was taken, the suspension filtered, the cake washed twice with acidic brine followed by hot water until the filtrate was clear. The washed cake was

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dried, weighed and analysed for As, Fe, Cu, C, elemental S and total S.

Experimental Results

The following experimental results were observed

5 Final Leach Solid Weight

Cake:

Wet cake + paper + filter paper: 744.27

Dry cake + paper + filter paper: 490.96

Paper + filter paper: 66.09

10 Dry cake obtained: 424.87

Mass reduction: 15 %

Solid Analysis feed to Pyrite Oxidation with Oxygen
Information in dry wt % or ppm as noted

Description	Fe	As	Cu	Au	S _t	S _e
	(%)	(%)	(%)	ppm	(%)	(%)
Total	4.31	0.55	0.61	-	-	-
Soluble	0.01	0.03	0.10	-	-	-
Insoluble	4.30	0.51	0.51			

15 Solid Analysis residue from Pyrite Oxidation with Oxygen
Information in dry wt % or ppm as noted

Description	Fe	As	Cu	Au	S _t	S _e
	(%)	(%)	(%)	ppm	(%)	(%)
Total	0.52	0.19	0.35	-	-	-
Soluble	0.01	0.01	0.01	-	-	-
Insoluble	0.51	0.18	0.34	-	-	-

20 Fe & As Extraction from Concentrate to Pyrite Oxidation residue

Both As and Fe extraction exceeded 95% as demonstrated in the following tables:

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Ref#	Mins	Sample (#)	T (°C)	O ₂ (Vmin)	Rh mV	pH	Cu (gpl) AA	Fe (gpl) AA	Fe (gpl) ICP	As (gpl) ICP	Cu (gpl) ICP	Comments
0	0	1	82	0.5	645	0.82	-	0	0	0	20	Added conc
1	30	2	91	0.5	570	0.82	-	0.15	0.21	0.08	18	
2	60	3	90	0.5	572	0.82	-	0.22	0.29	0.10	18	Frothing too much
3	90	-	88	0.5	580	0.91	-	-	-	-	-	
4	120	-	87	0.5	577	0.92	-	-	-	-	-	
5	150	-	83	0.5	580	1.01	-	-	-	-	-	
6	180	4	88	0.5	570	0.95	-	0.39	-	-	18	
7	210	-	91	0.5	580	0.95	-	-	-	-	-	
8												Stopped and transferred into 1L Added 5 litre of fresh solut
9												Vol= 15 litres

Ref#	Mins	Sample (#)	T (°C)	O ₂ (Vmin)	Rh mV	pH	Cu (gpl) AA	Fe (gpl) AA	Fe (gpl) ICP	As (gpl) ICP	Cu (gpl) ICP	Comments
1	0	1	101	1	530	0.9	18.5	0.5	0.6	0.13	18.1	
2	30	-	104	1	582	1	-	-	-	-	-	
3	60	-	105	1	585	0.95	-	-	-	-	-	
4	90	-	105	1	585	0.97	-	-	-	-	-	
5	120	-	105	1	583	1.07	-	-	-	-	-	
6	150	-	105	1	582	1.14	-	-	-	-	-	
7	180	2	108	1	593	1	18.8	0.9	1.0	0.19	18.6	
8	210	-	103	1	599	1	-	-	-	-	-	
9	240	-	105	1	600	0.95	-	-	-	-	-	
10	270	-	105	1	585	0.93	-	-	-	-	-	
11	300	-	103	1	600	0.93	-	-	-	-	-	New pH probe. The old one app arently as there was hardly any
12	360	3	102	1	610	<0.1	19.8	1.2	1.5	0.25	21.2	
13	390	-	102	1	609	<0.1	-	-	-	-	-	
14	420	4	105	1	606	<0.1	21	1.3	1.6	0.27	21.6	
15	450	-	105	1	616	<0.1	-	-	-	-	-	
16	480	5	105	1	614	<0.1	20.9	1.4	1.5	0.26	19.9	
17	480	-	105	1	605	<0.1	-	-	-	-	-	
18	540	-	105	1	625	<0.1	-	-	-	-	-	
19	570	-	105	1	630	<0.1	-	-	-	-	-	
20	600	6	105	1	627	<0.1	26.2	1.8	1.7	0.33	24.4	
21	630	-	105	1	630	<0.1	-	-	-	-	-	
22	660	7	105	1	629	<0.1	27.1	1.8	1.9	0.34	25.1	
23	690	-	105	1	622	<0.1	-	-	-	-	-	
24	720	-	105	1	624	<0.1	-	-	-	-	-	
25	750	8	105	1	625	<0.1	25.2	1.8	1.7	0.31	23.2	
26	810	-										
27												

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Pyrite oxidation, feed vs. residue:

	Wt %		Mass (g)	
	Feed	Residue	Feed	Residue
			500	424.9
Fe	4.3	0.51	21.6	2.2
As	0.5	0.18	2.6	0.8

Equivalent Concentrate

5

	Mass (g)	Concentration (%)
	535.2	100
As	17.1g	3.2
FeAsS	37.2	7.0
Fe	46.0	8.6
FeS ₂	25.6	4.8
S	29.4	5.5
S in FeAsS	7.3	1.4
S in FeS ₂	22.1	4.1
Fe in AsFeS	12.8	2.4
Fe in FeS ₂	19.3	3.6
Fe other	14.0	2.6

Fe and As extraction from Concentrate to Pyrite Oxidation residue:

Fe	95.3%
As	95.5%

10

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Extraction of elemental sulphur from the pyrite oxidation residue demonstrated the S(e) is equivalent to the S associated with the $AsFeS$ or 1.4 % in the concentrate

5

Elemental Sulfur		
Extraction		
Float Head Sample		
weight	8.68 g	100%
S(e) extraction		
residue		
Total	0.35 g	
Carbon	0.21 g	
S(e)	0.14 g	1.6%
Mass Change		79%
S(e) related to		
concentrate		1.28%

Now that preferred operating details of the process have been exemplified, it will be appreciated by those skilled in the art that the method of the present invention includes the following advantages:

- The method can be employed to recover precious metals from sulfidic ores and concentrates which are otherwise difficult or impossible to treat using conventional available processes/techniques such as smelting and roasting.
- The method can accommodate a high carbon content in such ores, because the method is conducted in solution, and thus blinding agents can be employed to prevent precious metal adsorption onto carbon, which can otherwise interfere with precious metal recovery.

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- The method can be employed to remove contaminants from a wide variety of ore and concentrate feedstocks which, once removed, can then be treated using conventional smelting/roasting techniques.
- 5 • In this regard, the method enables removal of arsenic, iron and sulfur in readily disposable forms from an original arsenopyrite concentrate, leaving a readily treatable concentrate.
- The method has the capacity to recover a wide variety of
10 metals of economic value, especially precious metals, using simple non-cyanide based leaching and separation processes, and including activated carbon adsorption.
- The method can be used to treat contaminated residues to
15 allow them to be subsequently disposed of with reduced environmental impact.

Whilst the invention has been described with reference to a number of preferred embodiments, it should be appreciated that the invention can be embodied in many other forms.

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CLAIMS

1. A method of removing a contaminant from a sulfidic material comprising the steps of:
 - mixing the material in an aqueous solution wherein a multi-valent species of a relatively high oxidation state oxidises the contaminant to render it soluble in the solution, produces a contaminant refined material, and is reduced to a relatively lower oxidation state; and
 - removing the contaminant from the solution whilst regenerating the multi-valent species to its relatively high oxidation state.
2. A method of removing a contaminant from a sulfidic material comprising the steps of:
 - mixing the material in an aqueous solution having an oxidation potential controlled to oxidise substantially only the contaminant to render it soluble in the solution, thereby producing a contaminant refined material; and
 - separating the solution from the contaminant refined material.
3. A method as claimed in claim 1 or 2 wherein the contaminant is removed from the solution by precipitation through the introduction of an oxidant into the solution in a precipitation stage.
4. A method as claimed in claim 3 when dependant on claim 1 wherein the oxidant simultaneously causes the multi-valent species to be oxidised to its relatively high oxidation state.
5. A method as claimed in claim 4 wherein, after precipitating and removing the contaminant and regenerating the multi-valent species to its higher oxidation state, the solution is recycled to the mixing stage.
6. A method as claimed in any one of claims 3 to 5 wherein in the precipitation stage the solution pH is maintained at around pH 2-3.

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7. A method as claimed in claim 6 wherein the solution pH is maintained by regulating the supply to the solution of the oxidant and/or an alkali agent.
8. A method as claimed in any one of the preceding claims wherein the contaminant is oxidised in a single or multi stage leaching process.
9. A method as claimed in claim 8 wherein the leaching process comprises a first leaching stage in which the oxidation potential is controlled to oxidise substantially only the contaminant to render it soluble in the solution, and a second leaching stage in which the oxidation potential is increased to oxidise sulfide in the contaminant refined material.
10. A method as claimed in claim 9 wherein the sulfidic material is a pyritic material, and in the first leaching stage the contaminant is oxidised at a solution Eh sufficient to oxidise the contaminant and leach it into solution but not substantially leach pyrite.
11. A method as claimed in claim 10 wherein in the first leaching stage the solution pH is less than 1, the solution Eh is around 0.5 volts, and the solution temperature is around 105°C.
12. A method as claimed in any one of claims 9 to 11 wherein the sulfidic material is a pyritic material, and in the second leaching stage the pyritic material is oxidised at a higher solution Eh than the first leaching stage, the Eh being sufficient to leach pyrite.
13. A method as claimed in claim 12 wherein the solution pH is less than 1, the solution Eh is around 0.6 volts, and the solution temperature is about 105°C.
14. A method as claimed in claim 12 or 13 wherein to achieve the higher solution Eh in the second leaching stage an oxidant such as oxygen, air, chlorine gas, or hydrogen peroxide is added to the solution.
15. A method as claimed in any one of claims 12 to 14 wherein in the second leaching stage a low pH in the

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solution is maintained by adding thereto an acid such as sulphuric acid or hydrochloric acid.

16. A method as claimed in any one of claims 9 to 15 wherein solution is separated from the material after each leaching stage for removal of contaminant therefrom.
17. A method as claimed in claim 16 wherein the separated solution from each leaching stage is combined, and contaminant is removed from the combined solution by precipitation in a manner as defined in any one of claims 3 to 7.
18. A method as claimed in claim 16 or 17 wherein contaminant refined material that is separated from the solution after the first leaching stage is fed to the second leaching stage.
19. A method as claimed in any one of the preceding claims wherein the aqueous solution includes a dissolved metal chloride.
20. A method as claimed in claim 19 wherein the chloride concentration is approximately 7 moles/litre.
21. A method as claimed in claim 19 or 20 wherein the metal in the dissolved metal chloride functions as the multi-valent species.
22. A method as claimed in claim 21 wherein the metal in the metal chloride is copper or iron.
23. A method as claimed in claim 22 wherein in the higher oxidation state the metal is Cu(II) or Fe (III) and in the lower oxidation state the metal is Cu(I) or Fe (II).
24. A method as claimed in any one of the preceding claims wherein the sulfidic material is a pyritic ore or concentrate.
25. A method as claimed in any one of the preceding claims wherein the contaminant is arsenic, antimony or bismuth present in the sulfidic material.
26. A method as claimed in any one of the preceding claims wherein after removing the contaminant the solution is recycled to the leaching stage.

27. A method as claimed in any one of the preceding claims wherein the sulfidic material comprises, in addition to the contaminant, a metal to be recovered, the method further comprising a metal recovery stage to recover metal from the separated contaminant refined material.
28. A method as claimed in claim 27 wherein a separate metal recovery stage is provided after contaminant oxidation, and additionally or alternatively is provided in-line prior and/or subsequent to contaminant precipitation.
29. A method as claimed in claim 27 or 28 wherein the sulfidic material is a double-refractory ore, and the metal recovery stage is provided as a separate, subsequent stage, to recover metal present in contaminant refined material solids from the leaching process.
30. A method as claimed in claim 29 wherein the metal recovery stage comprises a conventional roasting or smelting process to which the contaminant refined material solids from the leaching process is fed.
31. A method as claimed in claim 30 wherein chlorine or cyanide leaching is employed after roasting to recover any remaining metal in the roasted solids material.
32. A method as claimed in claim 27 or 28 wherein the sulfidic material is a single refractory ore and the metal recovery stage is provided in-line and subsequent to contaminant precipitation.
33. A method as claimed in claim 32 wherein metal recovery involves adsorption of the metal in solution onto carbon in a column containing activated carbon.
34. A method as claimed in any one of claims 27 to 33 wherein the metal is a precious metal such as gold, silver, platinum or other platinum group metal.
35. A method as claimed in any one of claims 27 to 34 wherein after a first leaching stage the solution is subjected to a thickening stage to thicken and separate contaminant refined material from the solution.

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36. A method as claimed in any one of claims 27 to 35 wherein after a second leaching stage the contaminant refined material is filtered from the solution for metal recovery or disposal.
- 5 37. A method as claimed in any one of claims 27 to 36 wherein the contaminant is filtered from the solution after contaminant precipitation and prior to in-line metal recovery.
- 10 38. A method of removing arsenic from a gold-bearing pyritic material comprising the steps of:
- leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride solution in which the metal has a relatively high oxidation state, such that the metal oxidises the arsenic
 - 15 to render it soluble in the solution, produces a pyritic material refined of arsenic, and is reduced to a relatively lower oxidation state;
 - precipitating and separating the arsenic from the solution in a precipitation stage whilst simultaneously
 - 20 regenerating the metal to its relatively high oxidation state; and
 - returning the solution to the leaching stage with metal in its relatively high oxidation state.
- 25 39. A method as claimed in claim 38 which is otherwise as defined in any one of claims 2 to 37.
40. A method of removing arsenic from a gold-bearing pyritic material comprising the steps of:
- leaching the material in a leaching stage wherein the material is mixed with an acidic aqueous metal chloride
 - 30 solution having an oxidation potential controlled to oxidise substantially only the arsenic to render it soluble in the solution, thereby producing a pyritic material refined of arsenic; and
 - separating the solution from the refined pyritic material.
- 35 41. A method as claimed in claim 40 which is otherwise as defined in any one of claims 1 or 3 to 37.

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42. A method of treating a relatively high carbon content sulfidic material contaminated with a contaminant to allow recovery of a precious metal present with the material, comprising the steps of:

- 5 •leaching the material in an aqueous solution wherein the contaminant and metal are solubilised in the solution, whilst masking the carbon in the material to prevent precious metal adsorption thereon; and
recovering the precious metal from the solution.

- 10 43. Any metal produced by the method of any one of the preceding claims.

Dated this 2nd day of May 2003

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By its Patent Attorneys
GRIFFITH HACK

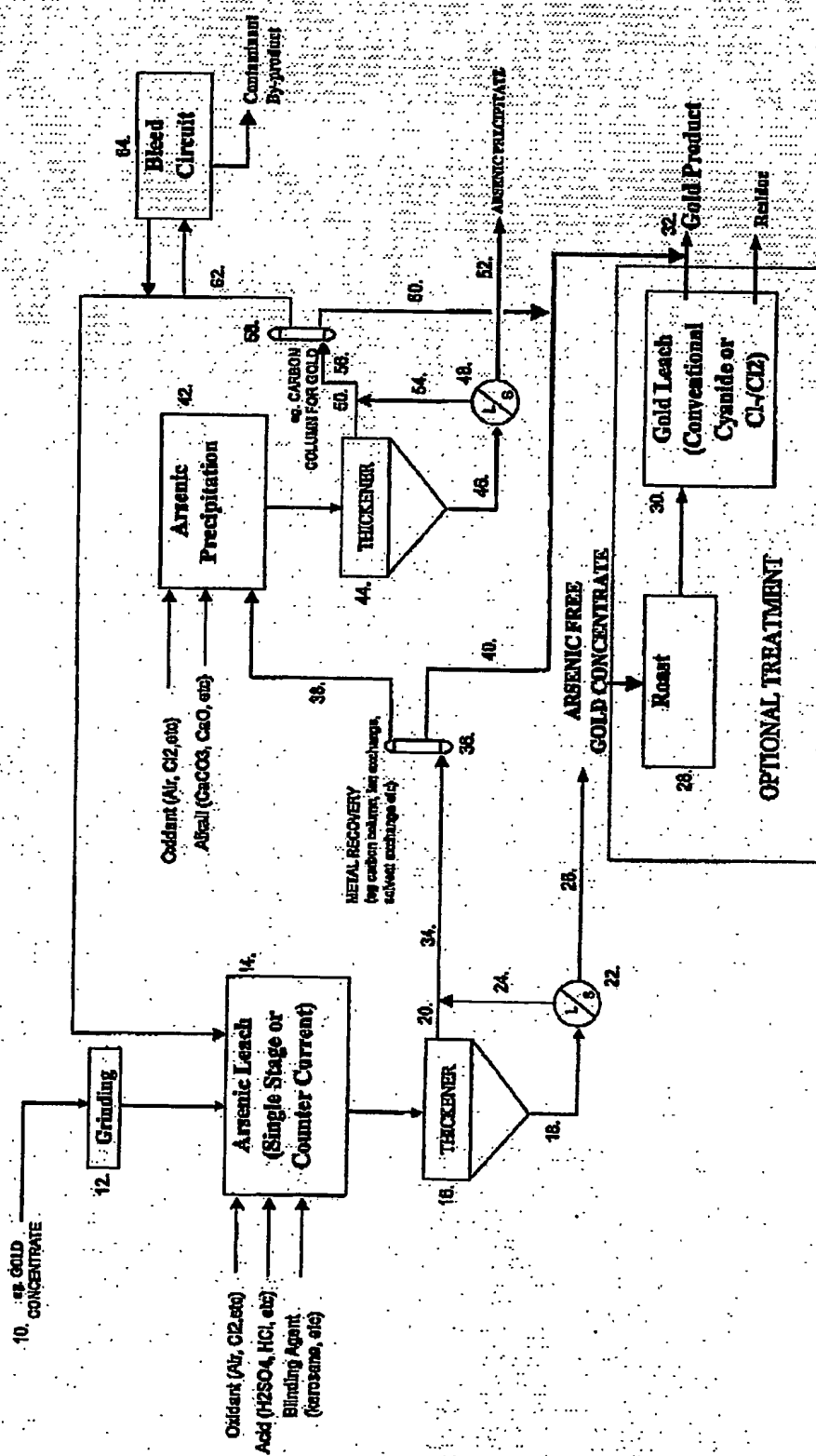


FIGURE 1

FIGURE 2

Flowsheet for Single-Refractory Gold Concentrates

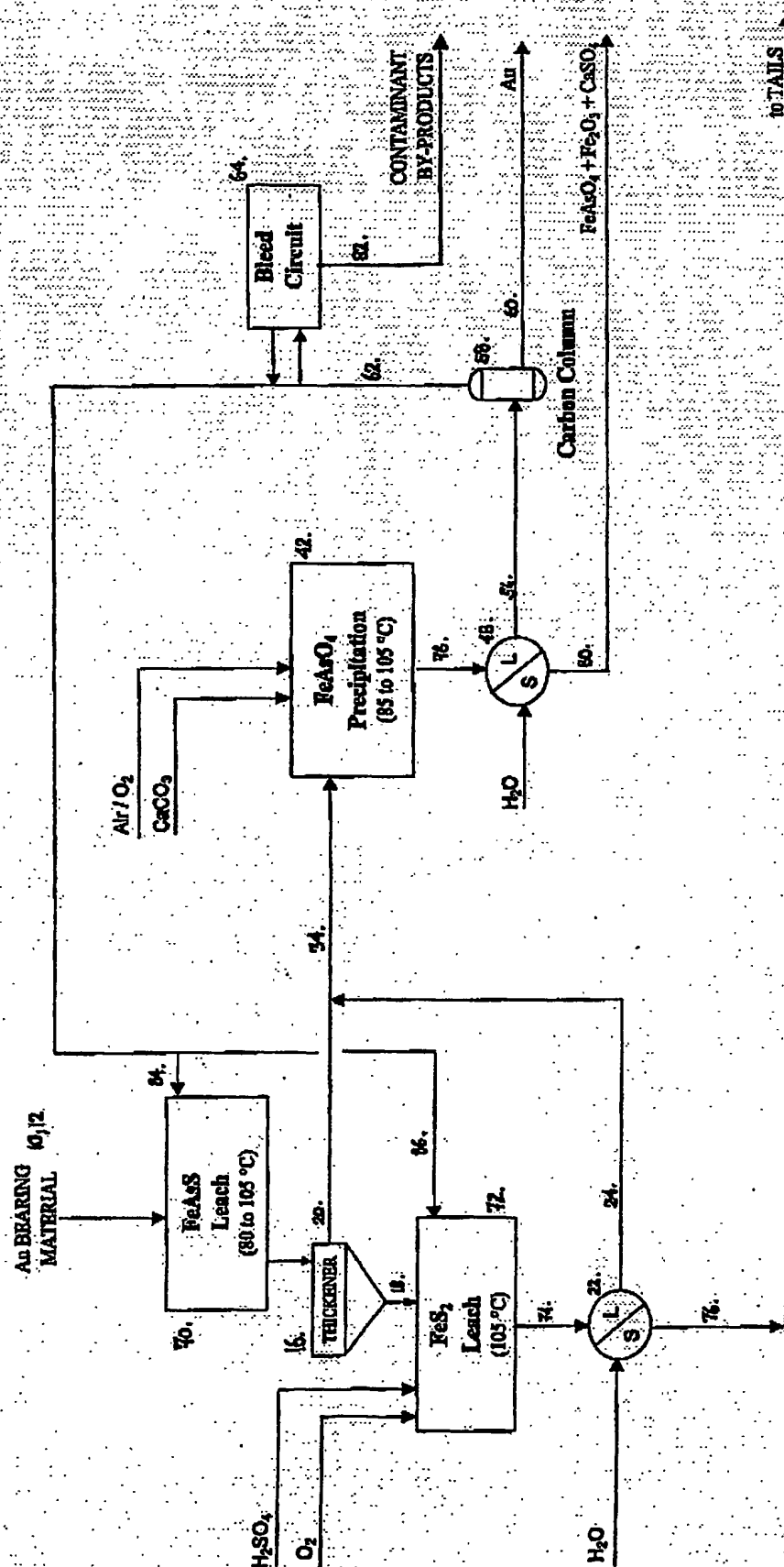


FIGURE 3
Flowsheet for Double-Refractory Gold Concentrates

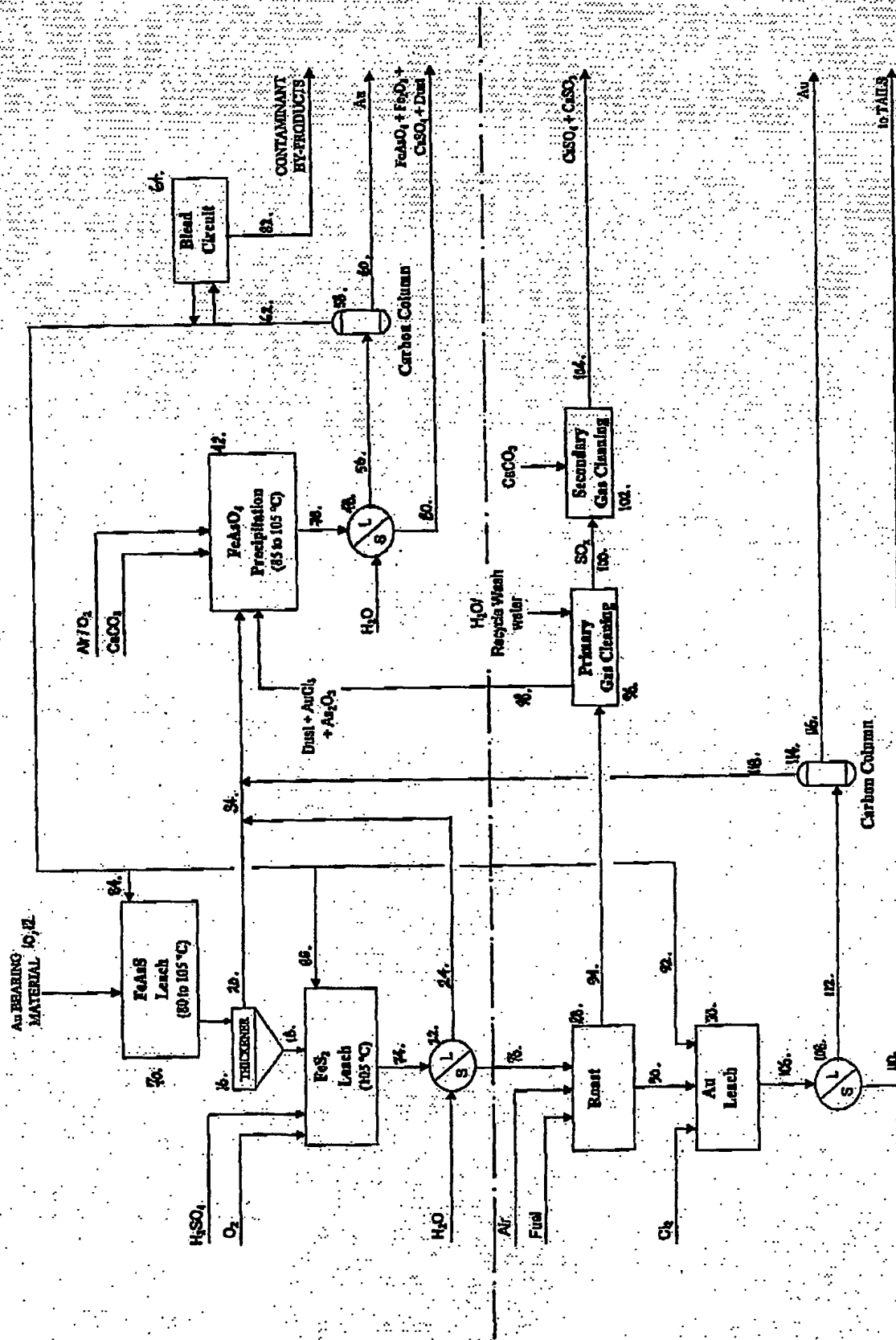


FIGURE 4
Continuous As Leach

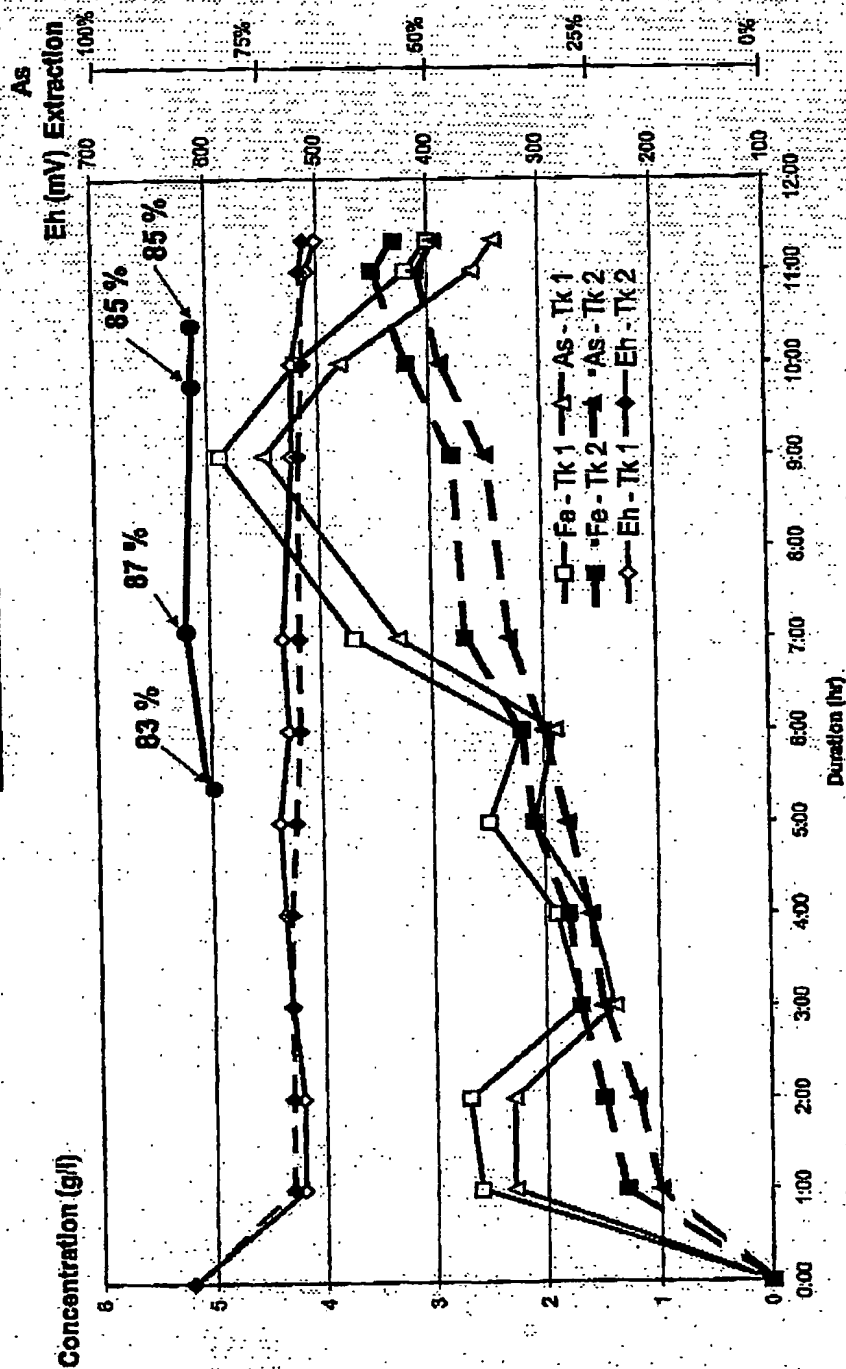
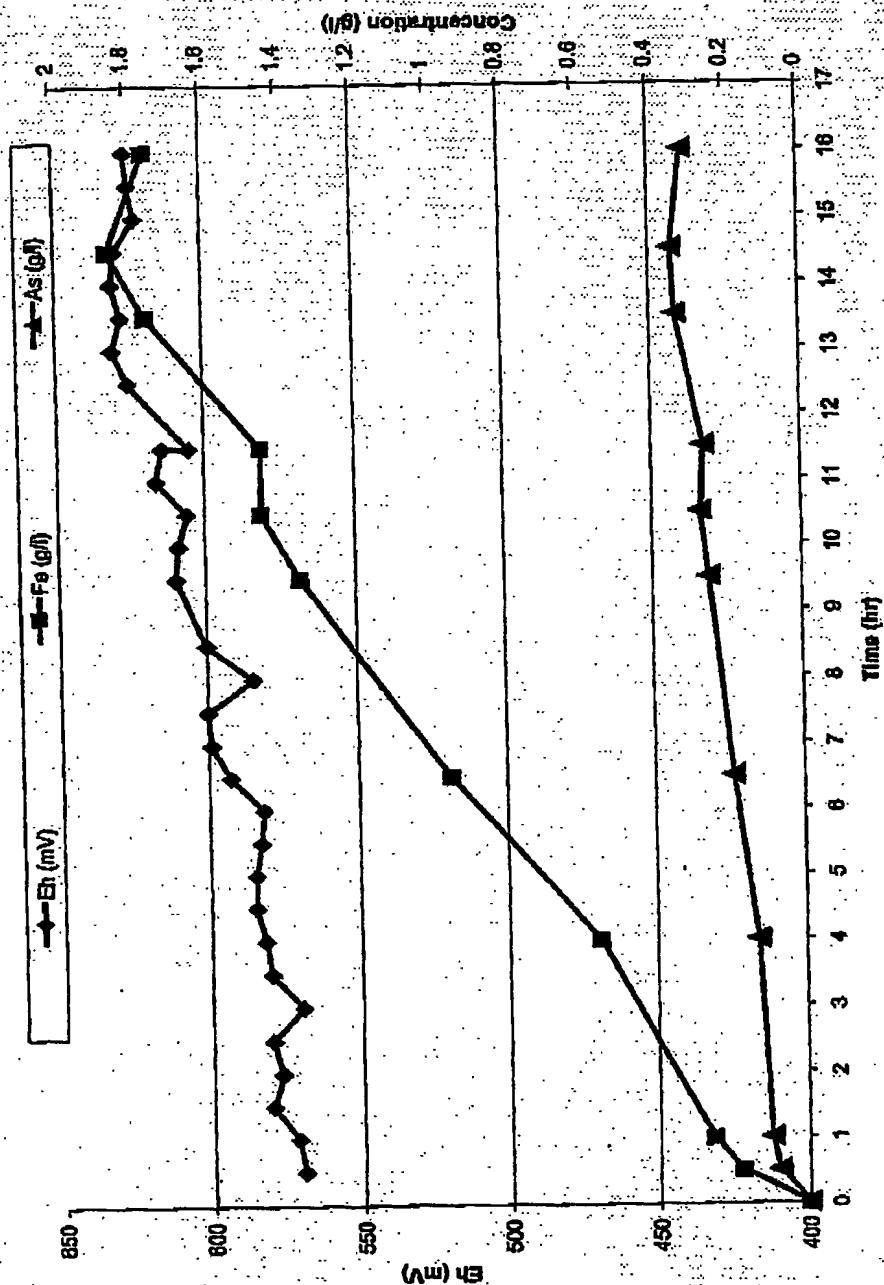


FIGURE 5**Pyrite Oxidation**

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